

MEASUREMENT AND INTERPRETATION OF ACID RAINFALL IN THE LOS ANGELES BASIN

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FINAL REPORT

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Abstract

The purpose of the work was to define the extent, degree and pertinent chemical characteristics of acid precipitation in the Los Angeles Basin of Southern California. Precipitation samplers were placed at nine locations: Pasadena, Azusa, Big Bear Lake, Central Los Angeles, Long Beach, Mt. Wilson, Riverside, Westwood and Wrightwood. A total of 533 individual samples were analyzed from the nine locations, and 38 different storms were sampled at one or more of the locations. Increments of precipitation collected during a storm were analyzed for pH, titration acidity, chloride, nitrate, nitrite, sulfate, fluoride, bromide, orthophosphate, total phosphate, bicarbonate, sodium, potassium, calcium, magnesium, ammonium, organic carbon and suspended solids.

The mean acidity in the Fall-Spring 1978-79 period ranged from a high of 38.4 μ equivalents/liter at Pasadena to a low of 2.45 μ equivalents/liter at Big Bear Lake, with corresponding mean pH's of 4.41 at Pasadena and 5.42 at Big Bear Lake.

At Pasadena, individual sample (0.25 inch increments of precipitation) acidities ranged from 1600 μ equivalents/liter to -8.1 μ equivalents/liter, and individual sample pH's ranged from 2.89 to 6.24. Incremental sampling during storms revealed significant changes in pH and chemical composition with time, with early stages of precipitation generally showing low pH and high nitrate and sulfate concentrations.

For the Fall-Spring 1978-79 period the mean ratio of nitrate to non-sea salt sulfate in precipitation varied from 0.4 at Long Beach to 2.8 at Big Bear Lake. The mean ratio at Pasadena was 0.9. Data on chemical composition of precipitation indicate that the observed net acidity is the

result of partial neutralization of the strong acids H_2SO_4 and HNO_3 by basic NH_3 and metal carbonates and oxides from soil dust. The relative extent of mixing of acids and bases varies considerably with location in the Basin. At Pasadena, mean Fall-Spring 1978-79 concentrations suggest that the net acidity, $38.5 \mu\text{eq}/\ell$, results from mixing of $31.4 \mu\text{eq}/\ell$ of HNO_3 , $35.6 \mu\text{eq}/\ell$ of H_2SO_4 , $21.1 \mu\text{eq}/\ell$ of NH_3 , and $7.4 \mu\text{eq}/\ell$ of alkalinity from soil dust.

Nitrate and nitrite in rainfall at Pasadena are correlated significantly with rainfall intensity, atmospheric ozone concentration and atmospheric nitric oxide concentrations. The same correlation is found for sulfate in rainfall. Inverse correlation of nitrates and sulfate with rainfall intensity is taken to reflect a rainfall dilution effect. For both nitrate and sulfate in rainfall a correlation is observed with Pb aerosol and total aerosol particulate matter.

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Disclaimer

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Summary and Conclusions

1. A total of 533 individual precipitation samples were collected at nine locations in the Los Angeles Basin between January 4, 1978 and March 29, 1979. Analysis of these samples has provided detailed data on the mean acidities, mean pH and mean chemical composition (chloride, nitrate, nitrite, sulfate, fluoride, bromide, phosphate, bicarbonate, sodium, potassium, calcium, magnesium, ammonium, and carbon) of precipitation at each of the nine locations sampled as well as information on the variation of acidity with time at given locations.
2. The mean acidities for the Fall-Spring 1978-79 season ranged from a high of 38.4 $\mu\text{equiv}/\ell$ at Pasadena to a low of 2.45 $\mu\text{equiv}/\ell$ at Big Bear Lake, with corresponding mean pH values of 4.41 and 5.42, respectively.
3. At Pasadena, the mean pH values over recent sampling periods were as follows:

September 1978 - March 1979	4.41
January 1978 - August 1978	4.47
September 1977 - December 1977	4.62
February 1976 - August 1977	4.06

The mean pH for 1976-77 reflects drought conditions. Higher mean pH values reflect greater rainfall (dilution effect).

4. The major components causing the net acidity in Los Angeles Basin precipitation are pollutant H_2SO_4 and HNO_3 . These acids are partially neutralized by gaseous NH_3 in the atmosphere and metal carbonates and

oxides from airborne soil dust, resulting in NH_4^+ and Ca^{2+} ions in the rainfall. Thus, the observed net acidities at different locations reflect transport from stationary and mobile pollutant sources, different atmospheric NH_3 levels over different parts of the Basin, and variations in amounts of alkaline soil dust with location.

5. Relative amounts of HNO_3 and H_2SO_4 in precipitation for the Fall-Spring 1978-79 period are given by the equivalent $\text{NO}_3^-/\text{SO}_4^{2-}$ ratio (corrected for sea salt), which varies with location as follows:

<u>Location</u>	<u>$\text{NO}_3^-/\text{SO}_4^{2-}$</u>
Long Beach	0.4
Westwood	0.7
Los Angeles	0.7
Mt. Wilson	0.7
Pasadena	0.9
Riverside	1.1
Azusa	1.3
Wrightwood	1.6
Big Bear Lake	2.8

6. Areal distribution of acidity in the Los Angeles Basin for the Fall-Spring 1978-79 period is characterized by lower pH and higher net acidity in the western Basin compared to eastern Basin and mountain location acidity, and by relatively higher proportions of nitric acid with respect to sulfuric acid as one progresses from coastal to central, eastern and mountain locations. Mean acidities at Pasadena, Westwood, Los Angeles and Long Beach for the Fall-Spring 1978-79 period were not

different at the 95% confidence level. Acidity at Pasadena was significantly greater than that at Riverside, Azusa, Mt. Wilson, Wrightwood and Big Bear. Acidity at Big Bear was significantly less than that of all other locations.

7. Acidity, pH, and chemical composition of rainfall can vary greatly with time and rainfall intensity during a storm at a given location. For example, at Pasadena pH variation from 4.05 to 4.69 within 5 hours and pH variation from 4.52 and 6.24 within about 12 hours have been observed. Correspondingly, nitrate and sulfate concentrations have been found to vary by more than twenty-fold within a given storm.
8. Low pH values (e.g., 2.89, 3.23, 3.70) were observed for small, early increments of rainfall after accumulation of acid components in the atmosphere.
9. Nitrate and sulfate concentrations in rainfall at Pasadena are significantly correlated with rainfall intensity, atmospheric ozone concentration, and atmospheric nitric oxide concentrations. Nitrate and sulfate in rainfall are also correlated with Pb aerosol and 1-hour total particulate matter.
10. Although total stationary and mobile emissions of NO_x and SO_x in the Basin are in an equivalent ratio of approximately 2.3 to 1, the local equivalent ratio of NO_3^- and SO_4^{2-} observed in precipitation varies from 0.4 at Long Beach to 0.9 at Pasadena to 2.8 at Big Bear Lake. Transport processes and relative rates of atmospheric scavenging and washout processes for HNO_3 and H_2SO_4 appear to have a strong influence on the chemistry of rainfall at different locations in the Basin.

Recommendations

1. The results of this study show clearly that the rainfall and snowfall in the Los Angeles Basin is acidic, i.e., pH less than 5.65. Only at an eastern mountain location, Big Bear Lake, is the mean pH approximately that of normal rainfall. Variations in pH can be great during storms, with early, low precipitation intensity values in the pH range 3-4 sometimes observed. It is important, therefore to focus attention on possible environmental effects of shorter-term, high acidity exposures in the environment, as well as on longer-term exposures to mean levels of acidity.
2. From mean acidities and mean precipitation rates at different locations in the Basin an estimate of the net flux of acidity to the Basin surface can be made. This estimate (2), suggests that on the order of 2% of the total equivalent acid-precursor emissions (NO_x and SO_x) reaches the surface of the Basin in precipitation (as net acidity from H_2SO_4 and HNO_3 and as weak acidity in the form of NH_4^+ salts). The remainder of the acidity emissions must reach the Basin surface as a dry flux via gas absorption (NO_x , SO_x) or as aerosol deposition (strong and weak acids in aerosol particles), become neutralized by oxidation-reduction processes, or be advected from the Basin as gases or aerosols. Perhaps on the order of 30% of the emitted acidity reaches the surface within the Basin as a dry flux (2). It is very important to obtain a fuller description of the dry flux, its temporal and spatial distributions, and the environmental effects associated with this kind of acid exposure.

3. Organic acids in Los Angeles area rainfall have been measured by Liljestrand (2). Concentrations of total organic acids were found generally to be less than 1 μ equiv/l. At Pasadena, concentrations of formic acid ranged from 0-50 nanomoles/l, acetic acid from 0-100 nanomoles/l and $> C_5$ acids from 0-100 nanomoles/l. Total organic carbon in the rainfall, however, varied from 0.5 to 4 mg/l, or from 40 micromoles/l to 330 micromoles/l. It seems important to extend identification and measurement of organic acids, and related organic species, in rainfall as a step in assessing possible environmental effects of other than strong acidity, e.g., H_2SO_4 and HNO_3 .

INTRODUCTION

Little information is available on the acidity of precipitation in the Western United States in general and in California in particular. The objective of the research reported here was to define the extent, degree and pertinent chemical characteristics of acid precipitation in the Los Angeles Basin of Southern California, a major metropolitan region with numerous fixed and mobile sources of atmospheric acids. To this end sequential rainfall samples (1/4-inch intervals) were collected at seven locations with the fifteen-month period from January 1, 1978 through March 31, 1979, and snowfall was sampled at two stations. Samples were analyzed for pH, titration acidity, nitrate, nitrite, sulfate, ammonium, chloride, fluoride, bromide, bicarbonate, sodium, potassium, calcium, magnesium, orthophosphate, total phosphate, organic carbon, and suspended solids.

The nine precipitation collection locations are indicated on Figure 1. Details of individual precipitation sampler locations are given in Table 1.

For each sampling site inclusive dates of sampling, number of storms sampled, number of individual precipitation samples, and total inches of precipitation sampled are summarized in Table 2. Sampling at Pasadena, Wrightwood, and Westwood was initiated in January 1978, while sampling at the six remaining locations commenced at a later date: fall 1978 or winter 1979. Conclusions on areal distribution of basin acidity are based on sampling during the Fall-Spring 1978-79 period. In addition, earlier sampling at Pasadena covered the period from February 1976 through December 1977 (1), providing a basis for comparison with the 1978-79 results.

Methods

Collection: Rainfall samples for inorganic analyses were obtained in an all-plastic collector which opened automatically at the beginning of precipitation and collected sequential 1/4-inch rainfall samples throughout a storm. Check-valve floats preserved integrity of samples prior to analysis. An all-glass and metal collector was used to collect samples for organic analyses. Figure 2 shows a drawing of the rainfall sampler (Model III of Liljestrang (2)).

Snow samples were collected in the mountains using a pre-cleaned plastic liner within a large plastic trash can. All samples at Big Bear Lake were snow samples; ninety percent of Wrightwood samples were snow. Snow samples were picked up within 3 to 5 days of event sampled.

Samples were stored at 4°C in the dark following collection and retrieval, until analyzed. Measurements of pH and conductivity were made in the laboratory within 24 hours of sample collection. Ammonia determinations were made within 48 hours of collection. Acidity titrations were performed within one week of collection. Anion analyses were made within two weeks of collection (except for samples collected during the period 1-78 through 6-78; because of heavy rainfall over this period, longer time periods were required before anion analyses). Metals were analyzed within six weeks of sample collection. A group of samples analyzed during and immediately following precipitation and again after three months of storage at 4°C in the dark showed no significant differences in results.

Laboratory Analyses: pH was determined in the laboratory electrometrically, using an Orion 801A digital pH/mV meter with a glass electrode-double junction reference electrode cell (Beckman Model AGU 39099 and Orion 90-02-00, respectively). The cell was calibrated with dilute solutions of strong acids to minimize junction potential effects.

Samples were titrated with standard base of concentration 0.001 N in a closed jacketed beaker in order to determine acidity. Initial pH was recorded, then high-purity nitrogen or argon was bubbled through the sample for 30 minutes to remove dissolved CO₂. The titration was carried out under a nitrogen atmosphere. Gran functions from the titration data

were plotted to distinguish strong and weak acid components (1). Results of such titrations (1,2) show that acidities in Los Angeles area samples consist of free acidity (H^+), dissolved carbon dioxide acidity ($H_2CO_3^-$), ammonium ion acidity (NH_4^+), and small amounts of weak acids such as organic acids ($RCOOH$) and hydrolyzable metals (e.g., Al^{3+} , Fe^{3+}). The net acidity, defined with respect to a pH datum of 5.65 (water in equilibrium with normal atmospheric CO_2) is essentially identical to free acidity ($[H^+]$), for our samples. Thus, laboratory pH measurements and acidity titrations yield concordant results.

A Dionex Model 10 ion chromatograph (3) was used for determining anion concentrations. A 100 μ l sample loop was used with 0.003M $NaHCO_3$ /0.0024 M Na_2CO_3 eluant, anion pre-column (#002106), anion separating column (#002176), and a suppressor column (#001802). Standard calibration curves were determined daily. For very dilute samples (e.g., snow samples from Wrightwood and Big Bear) an anion concentrator column was used, improving minimum detectable anion concentrations by a factor of forty.

The following anions were determined by ion chromatography: chloride, nitrate, nitrite, sulfate, fluoride, bromide, orthophosphate and bi-carbonate. In addition, fluoride was determined by the SPADNS method given in Standard Methods for the Examination of Water and Waste Water (4), total phosphate was determined spectrophotometrically (4), and chloride was determined by the method of Florence, et al. (5).

Ammonium, NH_4^+ , was determined in two ways: by means of an NH_3 electrode (Orion Ammonia Electrode 95-10) together with pH measurement; by the phenate standard method (4).

Metals were determined by Atomic Absorption Spectrophotometry (AAS) using a Varian AA-5 spectrophotometer. The following metals were determined by flame or carbon rod AAS, depending upon sample concentration: sodium, potassium, calcium, magnesium, iron, aluminum, manganese, nickel, lead and zinc. Metal ion standards were obtained from Harleco (2).

Silica (orthosilicic acid) was determined by the spectrophotometric method described by Strickland and Parsons (6).

Conductivity was determined on each sample using a Radiometer Model CDM2e conductivity meter. Total organic carbon was determined with a Dohrmann Envirotech Model DC-50 instrument. Suspended solids were determined gravimetrically after collection on a Whatman GF/C filter and heating to a constant temperature 103-105°C.

Uncertainties in acidities and other chemical characteristics are discussed in detail by Liljestr nd (2). Cross-calibration of ion chromatographic results with those obtained by earlier, standard methods has shown excellent correlations (Butler, et al.) (7).

The chemical data obtained in this study were subjected to three major consistency checks: (1) charge balance for all significant cations and anions determined; (2) conductivity balance between measured conductivity and that calculated from concentrations of all significant cations and anions; (3) comparison of strong acidity and weak acidity obtained from

acidity titration curves with the corresponding measured values of hydrogen ion, $[H^+]$, and ammonium ion, $[NH_4^+]$. (Other weak acids, e.g., hydrolyzable metals such as Fe^{3+} , or organic acids, such as $HCOOH$, were present at average levels of less than 5 μ equivalents/l.) Each of these tests showed excellent internal consistency in the analytical results obtained at each location and for the total of 533 samples.

The unusual precautions taken in cleaning sampling ware and in transferring and processing samples for laboratory analysis make it unlikely that artifacts arising from such processes as biological contamination, nitrification, or denitrification could significantly affect the results for pH, acidity, major anions and major cations. Re-analysis of selected stored samples yielded results not significantly changed over three months. Blanks were carried through the analytical procedures (one blank for twenty samples analyzed) as an additional assurance against sample alteration or contamination.

Overall, the uncertainties in reported pH values are perhaps ± 0.01 or ± 0.02 units (2 to 5% uncertainty). Uncertainties in anion and cation concentrations because of analytical variations are probably on the order of 5-10% for most of the analyses.

Results

Comparison of Acidities at Different Locations for Fall 1978-Spring 1979:

Table 3 lists the dates of sampling, the storms sampled, and the number of samples for the Fall 1978-Spring 1979 precipitation season at the nine locations in the basin. The fewest number of storms was sampled at Long Beach; the greatest at Westwood. Although the temporal coverages at the different stations are clearly not identical, it should still be useful to compare precipitation-weighted mean net acidities and pH values at the nine sampling locations during the Fall 1978-Spring 1979 period. The Fall 1978-Spring 1979 sampling period is probably a more representative one than the earlier (1976-78) periods sampled at Pasadena and a few other places in that the precipitation volume was only slightly above average and the temporal distribution was the typical one expected. Table 3 includes the mean pH values and mean acidities \pm a standard deviation for the nine locations. The means are precipitation-weighted values. The precipitation-weighted mean concentration is the flux of material, e.g., acidity, divided by the water flux, and is thus the average concentration corresponding to the average flux. The pH range and net acidity range for individual samples within all storms at a station are also given. (Negative acidity is alkalinity with respect to a pH 5.65 datum.)

Figure 3 presents these results as an areal distribution of mean pH and mean acidity values. The general impression gained from Figure 3 is that 1978-79 acidities tend to be lower in the eastern part of the basin and in the mountains and higher in the western and central parts of the basin.

In order to assess the significance of these areal variations in mean pH a pair-wise statistical comparison of the foregoing Fall 1978-Spring 1979 results was made for the nine sampling locations (8). Differences were characterized as: 1) not significant (less than the 95% confidence level); 2) significant at greater than the 95% confidence level; and 3) significant at greater than the 99% confidence level. Table 4 presents results of the comparisons. Differences in mean acidity were not significant between Pasadena and Westwood, Los Angeles, and Long Beach. There was a significant difference (99% level) in mean acidities between Pasadena and Azusa, Riverside, Mt. Wilson, Wrightwood and Big Bear. There was a significant difference (99% level) between acidity at Big Bear ($2.45 \pm 2.1 \mu \text{equiv/l}$, pH 5.422) and that at each of the other eight locations. Thus, there was a significant difference for the Fall 1978-Spring 1979 period in the acidities of the western basin (Westwood, Los Angeles, Pasadena, Long Beach) and the eastern basin and mountains (Riverside, Big Bear, Wrightwood, Mt. Wilson). Precipitation at the mountain sites had significantly less acidity than that at Azusa and the western basin sites.

Comparison of pH Values in Precipitation Increments at Nine Locations over an Extended Storm Period: The period from March 13 to March 21, 1979 experienced precipitation over the entire basin. pH and precipitation data were obtained for a large number of sequential samples at each of the nine sampling locations. A total of 52 samples were analyzed. We consider these

results as typical of the general pattern of areal distribution of acidity in the basin during the Fall-Spring period of 1978-79. The results are presented in Table 5, which gives the measured pH and volume of precipitation (inches) for each sample.

Mean Chemical Composition Data for Each Location: Precipitation-weighted mean results for individual cations: ammonium (NH_4^+), sodium (Na^+), potassium (K^+), calcium (Ca^{2+}) magnesium (Mg^{2+}) and hydrogen ion (H^+) and individual anions: chloride (Cl^-), nitrate (NO_3^-), sulfate (SO_4^{2-}), fluoride (F^-), bromide (Br^-), orthophosphate (H_2PO_4^-), and bicarbonate (HCO_3^-) for each sampling location are presented in Tables 6A through 14B. (Mean nitrite values are consistently low and hence are omitted.) Each table also gives the precipitation-weighted mean pH over the indicated sampling interval, the cation-anion charge balance (an indication of completeness and accuracy of analyses), the mean organic carbon content, mean total phosphate, and mean suspended solids content of all samples at each location. (Organic carbon, suspended solids, and total phosphate analyses are not available for Big Bear and Wrightwood.) For Pasadena, Westwood, and Wrightwood there were two sampling intervals: Winter-Summer of 1978 and Fall-Spring of 1978-79. The two intervals are reported separately (A and B) for each of these stations. (Comparisons with compositions at the other six stations use only the Fall-Spring data.)

Temporal Variations in pH, Nitrate, Sulfate, and Rainfall Intensity

During Representative Storms: Data obtained at Pasadena are representative of temporal variations in chemical composition of rainfall during storms. Observations for three events are presented which illustrate patterns of rainfall composition variation with time and intensity.

Table 15 presents data on intensity of precipitation, pH, NO_3^- , NO_2^- , and SO_4^{2-} at Pasadena for different times during a portion of a storm which spanned several days at the end of February and the beginning of March in 1978. The data are plotted in Figure 4. There are some evident qualitative correlations of rainfall intensity, nitrate, sulfate, and pH. (Individual nitrite values are, for the most part, low throughout the storm; a few high values occur in the early part of the storm.) This storm had high intensity periods in which acid constituents appear to be washed out, followed by periods of low intensity in which sea salt and soil dust components predominate. Then, nitric and sulfuric acid levels once again increase (early on March 1) and the pH falls once again.

Table 16 and 17 illustrate changes in pH, nitrate and sulfate during two storms of varying, moderate rainfall intensity at Pasadena in winter 1979. The data in Table 16 show a steady rise in pH, with corresponding decreases in nitrate and sulfate concentrations, over a two-day period of precipitation in January 1979.

For the two-day storm in February 1979 (Table 17), there is some tendency for pH to rise with time; definite fluctuations of pH later in the storm are associated with corresponding fluctuations in the nitrate and sulfate contents of the rainfall.

Extremely Low pH Values: The data for all stations occasionally show very low pH values for individual samples with correspondingly high values of sulfate and/or nitrate for these samples. These chemical results are typically associated with the first increments of rainfall. Examples from precipitation sampling at Pasadena serve to illustrate typical results for other stations exposed to high acidity. Table 18 presents pH, sulfate, and nitrate data for precipitation events in which a small increment of rainfall was collected following a period of no rainfall.

Correlations of Rainfall Chemistry and Air Quality Data: A multiple regression analysis was made for 198 individual precipitation samples collected at Pasadena to examine correlations between the quantities $[\text{NO}_3^-] + [\text{NO}_2^-]$ or $[\text{SO}_4^{2-}]$ in rainfall ([] denotes concentration in a rainfall sample) and the following variables: (1) HC, atmospheric hydrocarbon, (2) O_3 , (3) CO, (4) SO_2 , (5) NO, (6) NO_2 , (7) temperature, (8) relative humidity, (9) particulate matter, (10) rainwater hydrogen ion concentration, $[\text{H}^+]$, (11) $(\text{NO} \times \text{NO}_2)^{1/2}/[\text{H}^+]$, (12) $(\text{NO}_2)/[\text{H}^+]$ and (13) precipitation intensity, I. Air quality data in the foregoing set of variables, e.g., O_3 , ozone concentration, are available on an hourly-average basis from the Southern California Air Quality Management District (SCAQMD). Recording rain gauge data, to obtain variations in rainfall intensity values, were available only for the Pasadena site.

The multiple regression analysis indicates that the sum of nitrate and nitrite, $[\text{NO}_3^-] + [\text{NO}_2^-]$, is correlated, at greater than the 95 percent confidence level, with the following variables:

Precipitation Intensity, I

Atmospheric Ozone Concentration, (O_3)

Atmospheric Nitric Oxide Concentration, (NO)

$(NO)/[H^+]$

The strongest correlation is with precipitation intensity (which may perhaps be seen in simple terms as a dilution effect).

$[SO_4^{2-}]$ in rain water was found to correlate (95 percent confidence level) with the following variables:

Atmospheric Nitric Oxide, (NO)

Atmospheric Ozone, (O_3)

Precipitation Intensity, I

Aerosol composition data (24-hour averages) were available from SCAQMD for only 19 of the sampling dates on which at least 1/4 inch of rainfall was collected. In addition to the air quality variables considered above, the following aerosol characteristics were included in a multiple regression analysis for these 19 sampling dates: (a) 24-hour total particulate matter, (b) Pb aerosol, (c) nitrate aerosol, and (d) sulfate aerosol. The $[NO_3^-] + [NO_2^-]$ of rainfall for the set of samples was found to correlate at the 95 percent confidence level with:

Pb aerosol

$[SO_4^{2-}]$ in rainfall (dilution effect)

1-hour total aerosol particulate matter

O_3

$(NO_2)/[H^+]$

The $[\text{SO}_4^{2-}]$ of rainfall correlated (95 percent confidence level) with:

Pb aerosol

$[\text{NO}_3^-]$ in rainfall (dilution effect)

1-hour total particulate matter

O_3

$(\text{NO}_2)/[\text{H}^+]$.

Discussion

The overall sampling program to define the characteristics of precipitation acidity in the Los Angeles Basin covered a 15-month period from January 1978 through March 1979. For the rainy Fall-Spring season of 1978-79, samples were collected at nine locations (Table 1, Figure 1). The details of the total sampling coverage given in Table 2 show that 533 individual samples were collected and analyzed; 369 of these were obtained in Fall-Spring 1978-79. At Pasadena and Westwood, thirty-eight storms were sampled during the 15-month period. Shorter periods of sampling and fewer samples (Table 2) were involved for the seven other locations. As a result of the basin wide sampling program carried out in the Fall-Spring period of 1978-79 we have obtained a picture of areal distributions of mean acidities in the Los Angeles Basin, a definition of the range of pH and acidity at a number of locations, and sufficient information on the major ionic constituents of rainfall to provide a basis for relating observed net precipitation acidities to contributions from different kinds of sources, e.g., air pollutants and soil dust.

Areal Distribution of Precipitation Acidity: Areal distributions of rainfall acidities and pH for the Spring-Fall 1978-79 period (Figure 2, Table 3) show a high mean acidity at Pasadena, $38.4 \mu \text{equiv}/\ell$, and a low mean acidity at Big Bear Lake, $2.45 \mu \text{equiv}/\ell$. Acidities at western basin locations: Pasadena, Los Angeles, Westwood, and Long Beach are not significantly different at the 95 percent confidence level. The low mean acidity observed at Big Bear is significantly different, at the 95 percent confidence level or greater, from the acidities at each of the remaining eight locations. As a group, the western basin locations have higher acidities than the eastern basin and mountain locations. Acidity at Azusa is significantly lower than that at Pasadena, but is not significantly different from other western basin acidities. The general pattern of areal distribution inferred from the mean acidity and mean pH results is borne out by comparisons of pH values at the nine locations during individual storms. Table 5 shows generally lower pH values in the western basin and higher pH values in eastern and mountain locations during a winter 1979 storm.

Comparison of Pasadena Results over Time: Mean pH at Pasadena during January - August 1978 was 4.47; for September 1978 - March 1979 it was 4.41 (compare Tables 6A and 6B). Liljestr nd and Morgan (1) earlier found the mean rainfall pH at Pasadena to be 4.06 for the period September 1976 through September 1977. The mean acidity corresponding to this pH is significantly greater than the mean acidities observed in 1978-1979 sampling at Pasadena.

The mean pH values for four different sampling periods at Pasadena were as follows (Liljestrang (2)):

September 1978 - March 1979	4.41 (23.3 inches)
January 1978 - August 1978	4.47 (34.8 inches)
September 1977 - December 1977	4.62 (6.49 inches)
February 1976 - August 1977	4.06 (21.0 inches)

The principal reason for the difference is that the total amount of rainfall was at least two times greater for the later sampling periods than in 1976-77, which was a drought period. Thus, our recent observations on total acidity at Pasadena are qualitatively in accord with earlier results, when the influence of the overall dilution associated with greater rainfall is taken into account.

Chemical Composition and Types of Sources: The mean chemical composition data for each location in Tables 6A through 14B are valuable for identifying the relative influences of different source types on the precipitation chemistry. The major atmospheric components influencing the net amounts of several acid-base species in precipitation are believed to be the pollutant acids SO_2 and NO_x , the basic gas NH_3 and the metal carbonates and oxides of soil dust (1). In the rainfall, the resultant acids formed are H_2SO_4 , H_2SO_3 , HNO_3 , and HNO_2 which are partially neutralized by dissolved NH_3 and alkaline CaCO_3 particles, yielding NH_4^+ , $\text{CO}_2(\text{aq})$, HCO_3^- , NO_3^- and SO_4^{2-} (plus smaller concentrations of NO_2^- and HSO_3^-).

As an example, the data for Azusa (Table 7) show mean NO_3^- and SO_4^{2-} concentrations of 43.9 and 37.7 $\mu\text{eq}/\ell$, respectively. The net pollutant sulfate, after deducting the estimated contribution from sea salt, is 34.9 $\mu\text{eq}/\ell$. Thus, one can view the mean composition shown in Table 7 for Azusa as resulting from the mixing and neutralization of 43.9 $\mu\text{eq}/\ell$ of HNO_3 , 34.9 $\mu\text{eq}/\ell$ of H_2SO_4 , 36.2 $\mu\text{eq}/\ell$ of NH_3 , and approximately 20 $\mu\text{eq}/\ell$ of bases from soil dust (and, possibly, other alkaline sources).

In considering variations in mean chemical composition with location, certain qualitative patterns can be seen in the data for Fall through Spring 1978-79:

- (1) Sulfates, corrected for estimated sea salt contributions are highest at western basin locations (Long Beach, Los Angeles, Westwood), somewhat lower at central stations (Pasadena, Azusa, Mt. Wilson) and much lower at the mountain stations (Wrightwood, Big Bear). Figure 5 shows the pattern of mean non-sea salt sulfate for the Fall-Spring 1978-79 sampling period.
- (2) Nitrates are highest at Azusa; about equally high at Los Angeles, Pasadena, and Riverside; and lower at Long Beach, Mt. Wilson, and Big Bear. Lowest nitrate concentrations were found in the mountains at Wrightwood. Mean nitrates are shown in Figure 6.

- (3) Sodium, a sea salt tracer, is highest at the western, nearer-coastal locations: Long Beach, Los Angeles and Westwood. Sodium levels are quite low ($\sim 11\%$ of western basin values) at Wrightwood and Big Bear. Pasadena, Riverside, Azusa and Mt. Wilson have intermediate concentrations of sodium.
- (4) Ammonium levels are low at Long Beach, Westwood and Pasadena, and extremely low at Wrightwood. Highest ammonium values were found at Riverside, Los Angeles, Azusa and Mt. Wilson. An explanation for high ammonium levels at Los Angeles is not evident.
- (5) Calcium, a soil dust tracer, was highest at Riverside, Azusa and Los Angeles. (The high Los Angeles value may have been influenced by nearby construction.) The lowest calcium values were found at Wrightwood. Fairly uniform, intermediate calcium values were found for Westwood, Long Beach, Pasadena, and Mt. Wilson.

The ratio of equivalent NO_3^- concentration to equivalent SO_4^{2-} concentration (non-sea salt) is an indication of the relative importance of NO_x and SO_2 acid sources in the rainfall. Liljestr nd and Morgan (1) reported a value of 1.32 for this ratio for Pasadena rainfall in the period February 1976 to September 1977. The corresponding ratio for Fall-Spring 1978-79 rainfall at Pasadena is approximately 0.9 (calculated from Table 6B, correcting for the sulfate from seawater by using Na^+ as a tracer).

The approximate nitrate acidity to sulfate acidity ratios on an equivalent basis for the nine sampling locations during the Fall-Spring 1978-79 sampling periods are:

Long Beach	0.4
Mt. Wilson	0.7
Los Angeles	0.7
Westwood	0.7
Pasadena	0.9
Riverside	1.1
Azusa	1.3
Wrightwood	1.6
Big Bear Lake	2.8

It is interesting, as an example, to compare the acid characteristics of rainfall at Pasadena and Long Beach. As noted in Results (Table 4), the acidities and mean pH values for these two locations are not significantly different for the 1978-79 samples. The sum of equivalent nitrate and non-sea salt sulfate at Pasadena and Long Beach are almost the same, 67 and 66 $\mu\text{eq}/\ell$, respectively. At Long Beach, sulfuric acid accounts for about 70% of the strong acid sources; at Pasadena, sulfuric acid accounts for about 53%.

Thus, the areal distribution of acidity in precipitation is characterized by higher net acidity and lower pH in the western Los Angeles Basin compared to the eastern Basin and mountains, and by a shift toward higher nitric acidity relative to sulfuric acidity at central, eastern and mountain locations.

The free hydrogen ion concentration, $[H^+]$, at each location is determined almost entirely by the mixing and neutralization in rainfall (or in aerosol before precipitation) of H_2SO_4 , HNO_3 , NH_3 , and other soil-derived bases such as $CaCO_3$ and $MgCO_3$. Weak inorganic acids, e.g., those of fluoride, nitrite and sulfite appear to have little influence on the charge balance. Liljestrand (2) using chromatographic methods, found organic acid concentrations in rainfall samples at seven different locations to be less than $1 \mu\text{eq}/\ell$. This is consistent with our conclusion from acidity titrations that weak acids other than NH_4^+ amount to less than $5 \mu\text{eq}/\ell$ in all samples. Organic acids do not appear to be major components in the total acidity. (Further work is still needed to identify and quantitate individual organic acids in precipitation under a range of atmospheric conditions: levels of smog intensity and duration prior to rainfall.)

Temporal Variations in Acidity: Sampling of increments of rainfall within storms (Table 15) has revealed some striking temporal variations in concentration of acidity components, and their correlation with rainfall chemistry.

Other examples from sampling at Pasadena (Tables 16 and 17) are in accord with these observations. We expect that this pattern of temporal variation in acidity during storms is typical for other locations in the basin.

Our data also illustrate the very low pH values that can be observed for short, early increments of rainfall after accumulation of acid components in the gas or aerosol phase. Table 18 shows pH values from 2.89 to 3.87 found in small rainfall increments early in precipitation events. Long-term average pH values at the same location were in the 4.4 to 4.5 range.

Rainfall Chemistry and Air Quality: Predictive models successfully relating rainfall chemistry to air quality have not yet been developed. As a result of our incremental sampling work we have noted certain significant correlations, but we do not consider them to be of predictive value. The nitrate content of rainfall correlates quite strongly with precipitation intensity (as already noted in connection with Figure 3). Ozone concentrations and nitric oxide concentrations in air are also significantly correlated with nitrate in rainfall. The parameter $(NO)/[H^+]$, nitric oxide concentrations in air divided by hydrogen-ion concentrations in rainfall, which shows significant correlation with nitrate in rainfall, was chosen to describe a possible equilibrium dissolution process for NO gas in water.

The sulfate content of rainfall increments was found to be significantly correlated with NO concentrations in air, ozone in air, and precipitation intensity.

When longer-term aerosol data (24-hour averages) were added to the list of air quality variables and examined for correlations with rainwater nitrate and sulfate, Pb aerosol and 1-hour total particulate matter were found to be additional correlated variables for both nitrate and sulfate in rainfall.

The underlying physical-chemical features of these observed correlations will require more detailed studies of, e.g., in-cloud processes and aerosol washout. The resulting concentrations of H_2SO_4 in rainfall (from SO_2 , SO_3 , and H_2SO_4 of aerosol), and the resulting HNO_3 and HNO_2 in rainfall (from NO , NO_2 , HNO_3 and HNO_3 of aerosol) are brought about by a complex set of gas-liquid equilibrium and rate processes. Although the total emissions of NO_x and SO_x in the Los Angeles Basin are in an equivalent ratio of about 2.3, the precipitation-weighted mean ratio of NO_3^- to SO_4^{2-} in the rainfall for all nine locations Spring-Fall 1978-79 period is only about 0.8. The local ratio of NO_3^- to SO_4^{2-} in rainfall varies from about 0.4 (at the coast) to about 2.8 (in the eastern mountains). Clearly, the processes which bring about transfer of acidity from gas and aerosol to precipitation are in need of further study. Correlations of air quality data and rainfall composition data at particular locations do not yet appear to provide a basis for extrapolation to other conditions.

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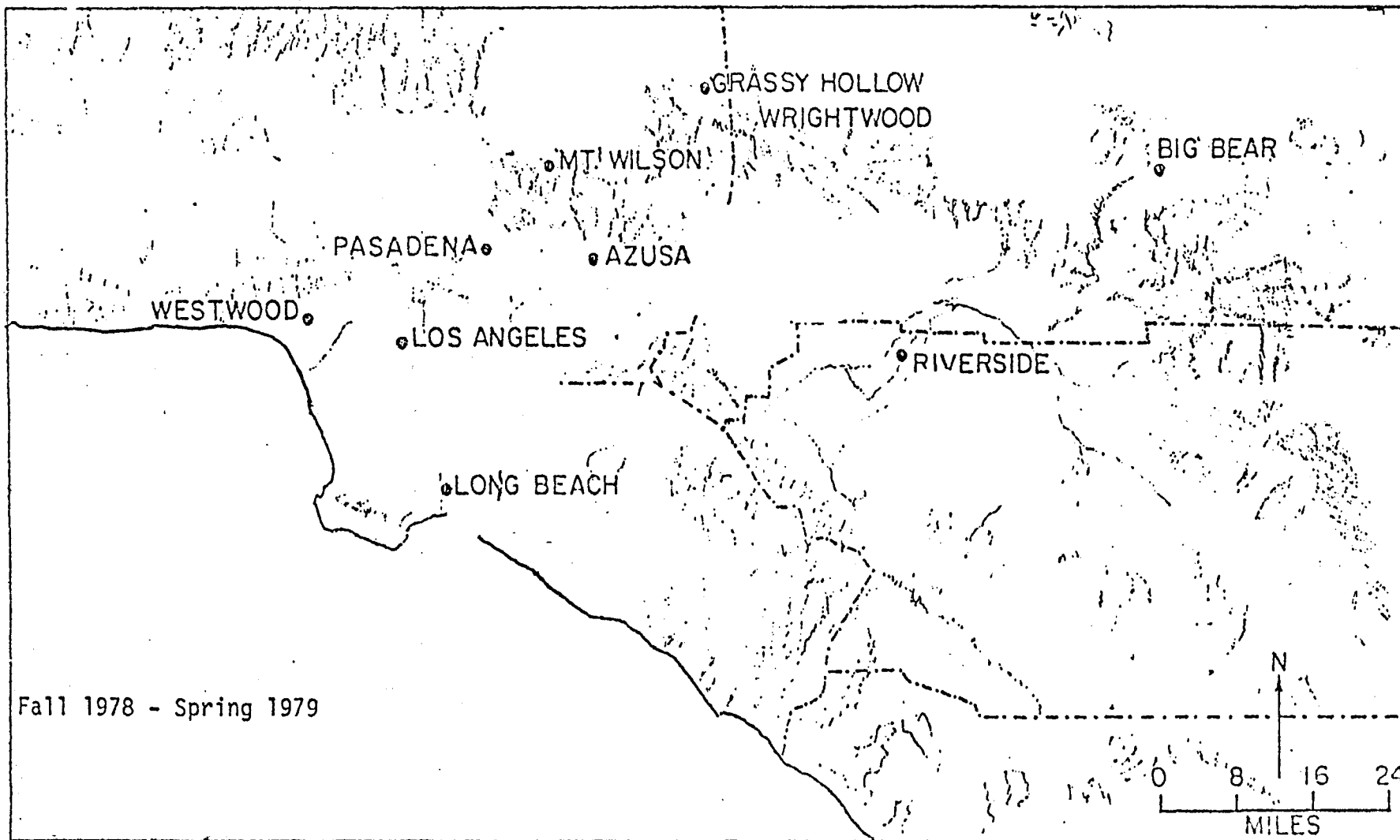
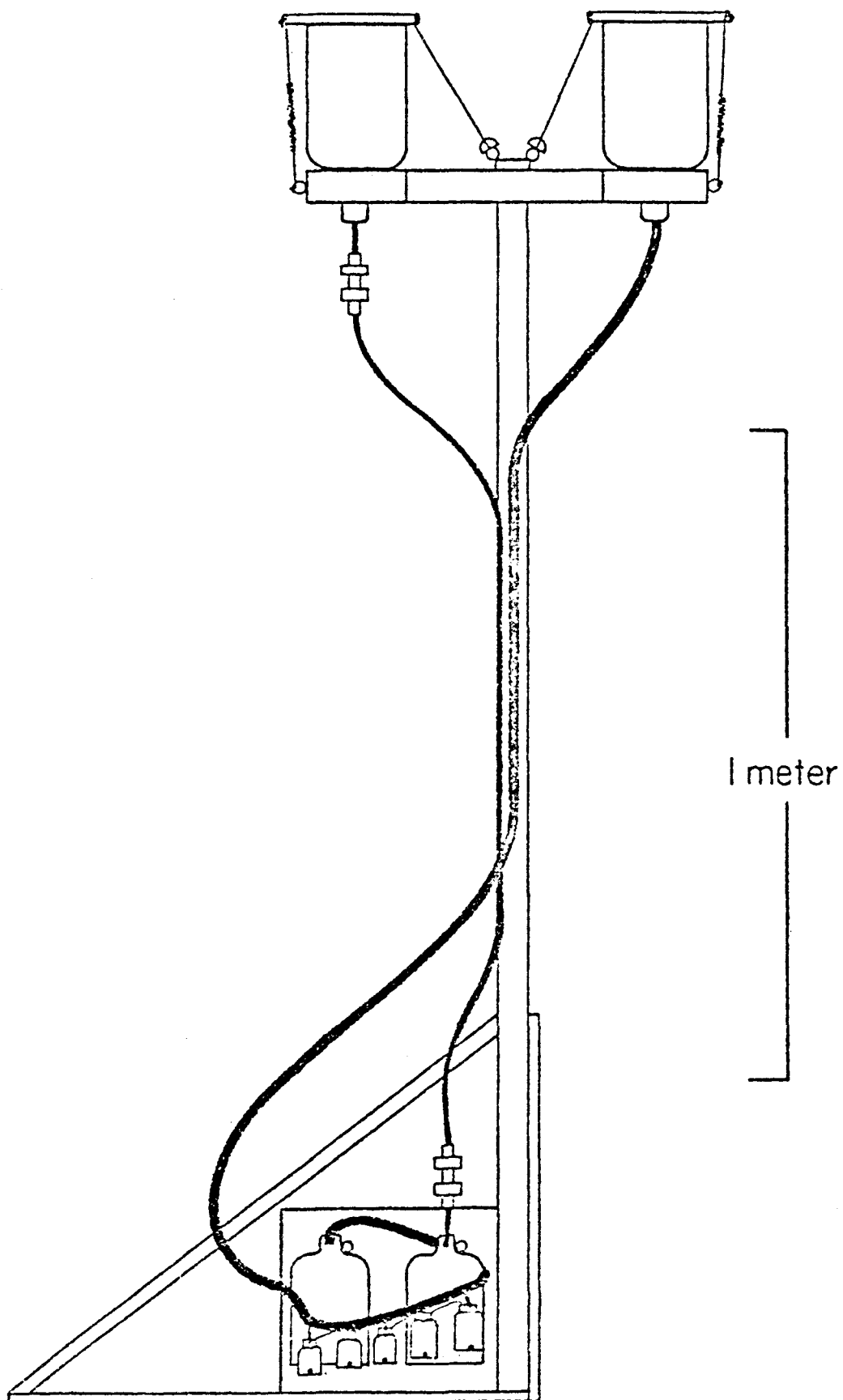


Figure 1. Precipitation Collection Location.

Figure 2. Rainfall Sampler.



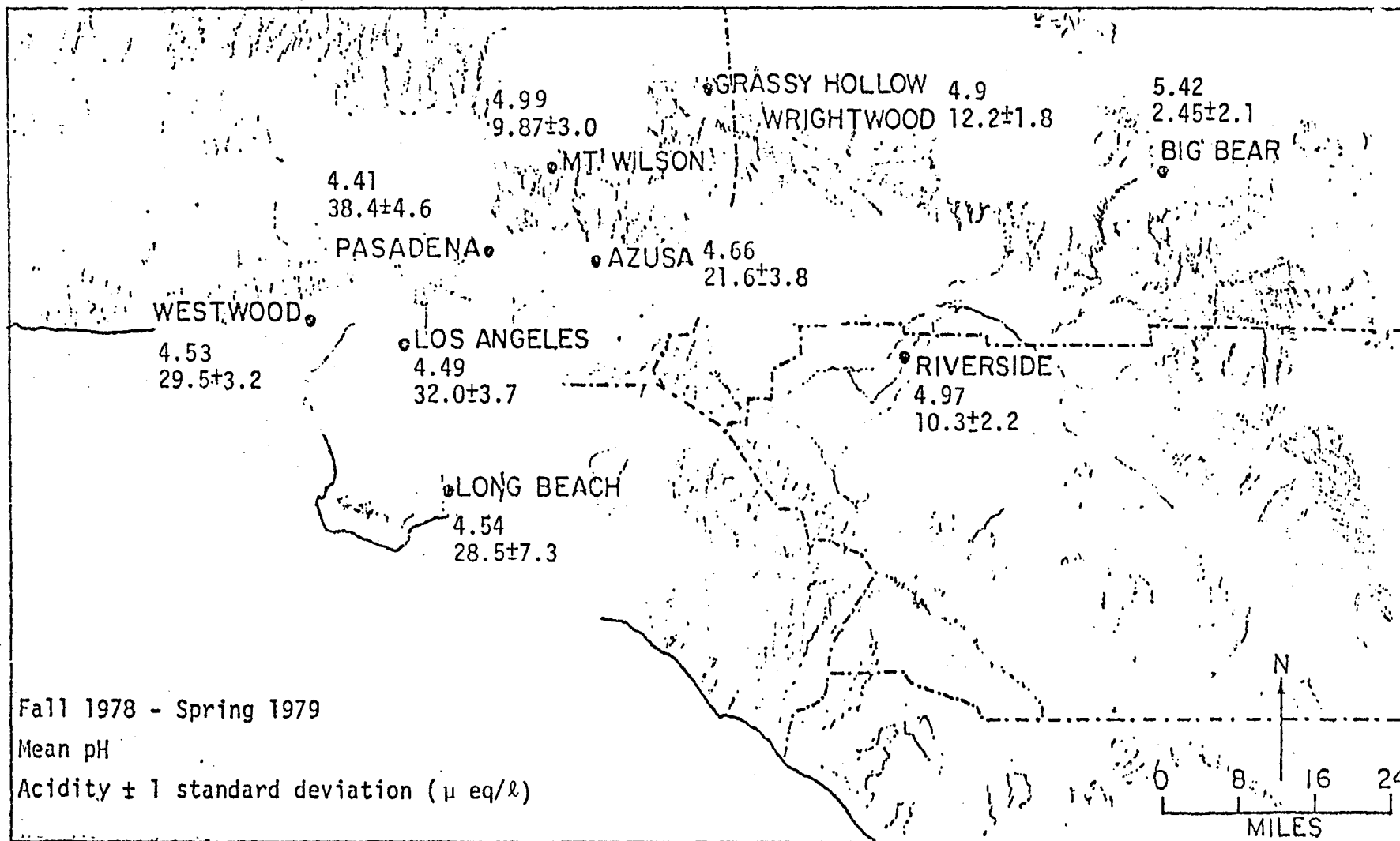


Figure 3. Mean pH and Mean Acidity Values.

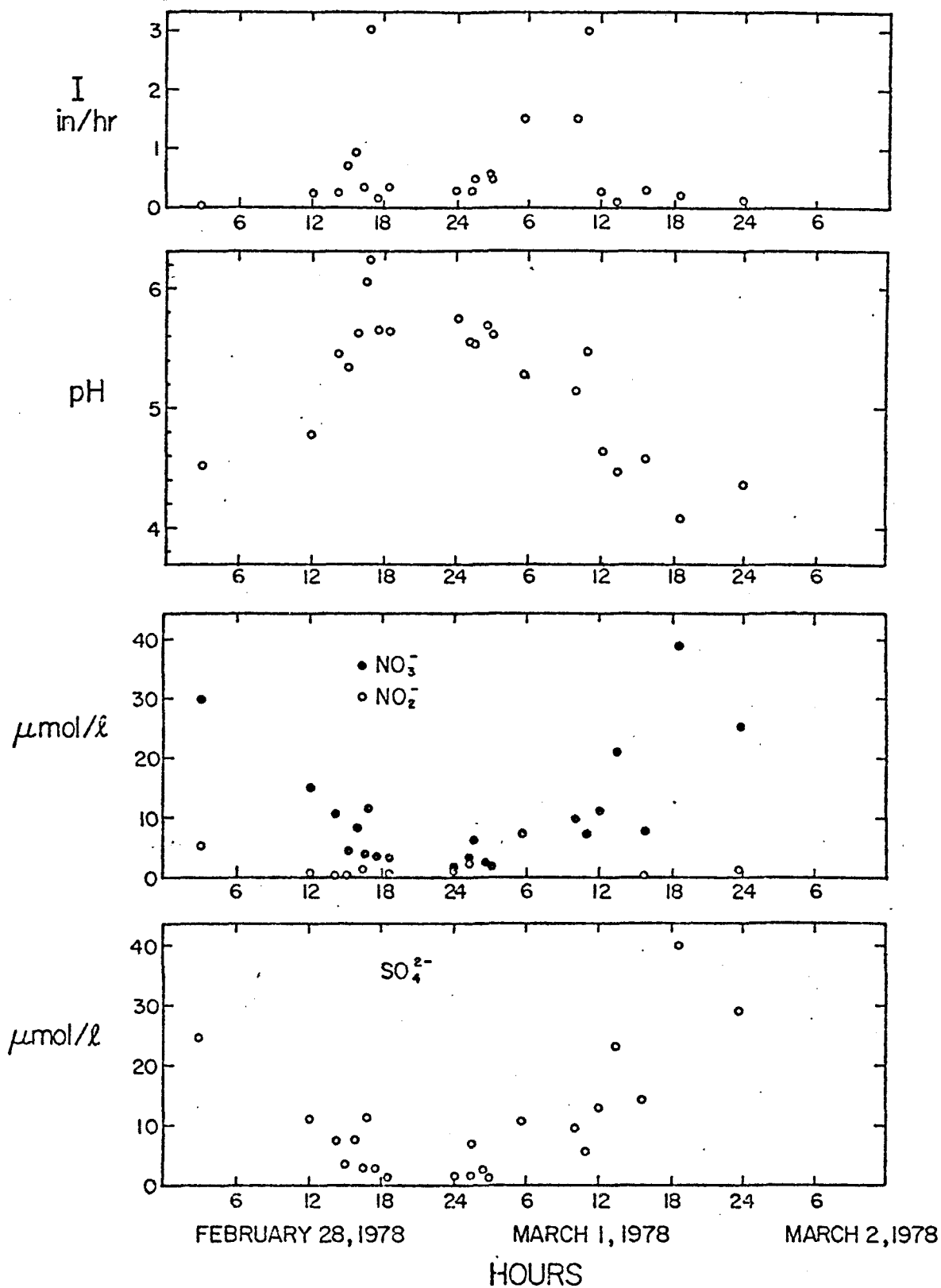


Figure 4. Variation of Rainfall Intensity, pH, Nitrate, and Sulfate During a Storm at Pasadena, February 28-March 2, 1978.

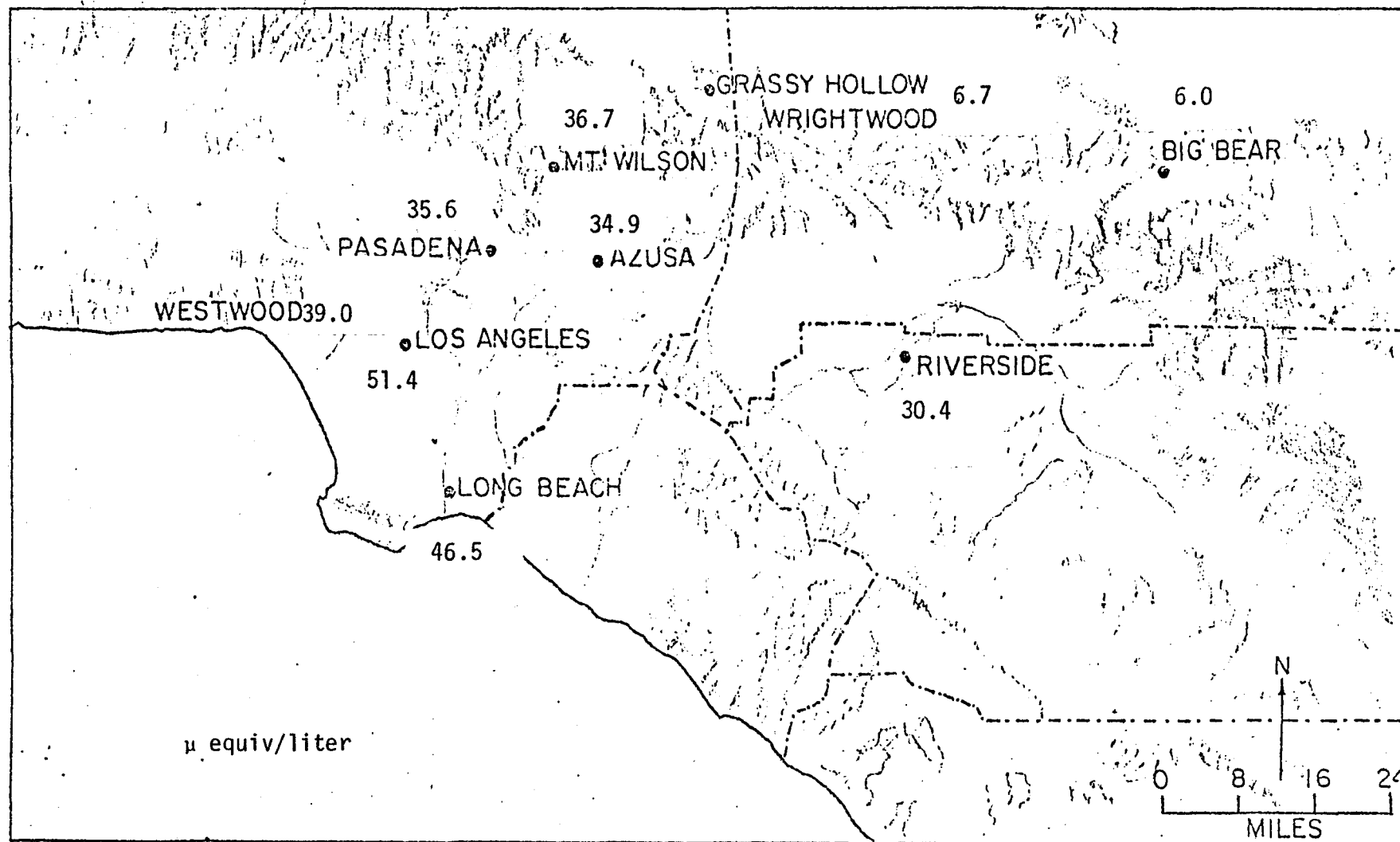


Figure 5. Mean Values of Non-Sea Salt Sulfate. Fall 1978-Spring 1979

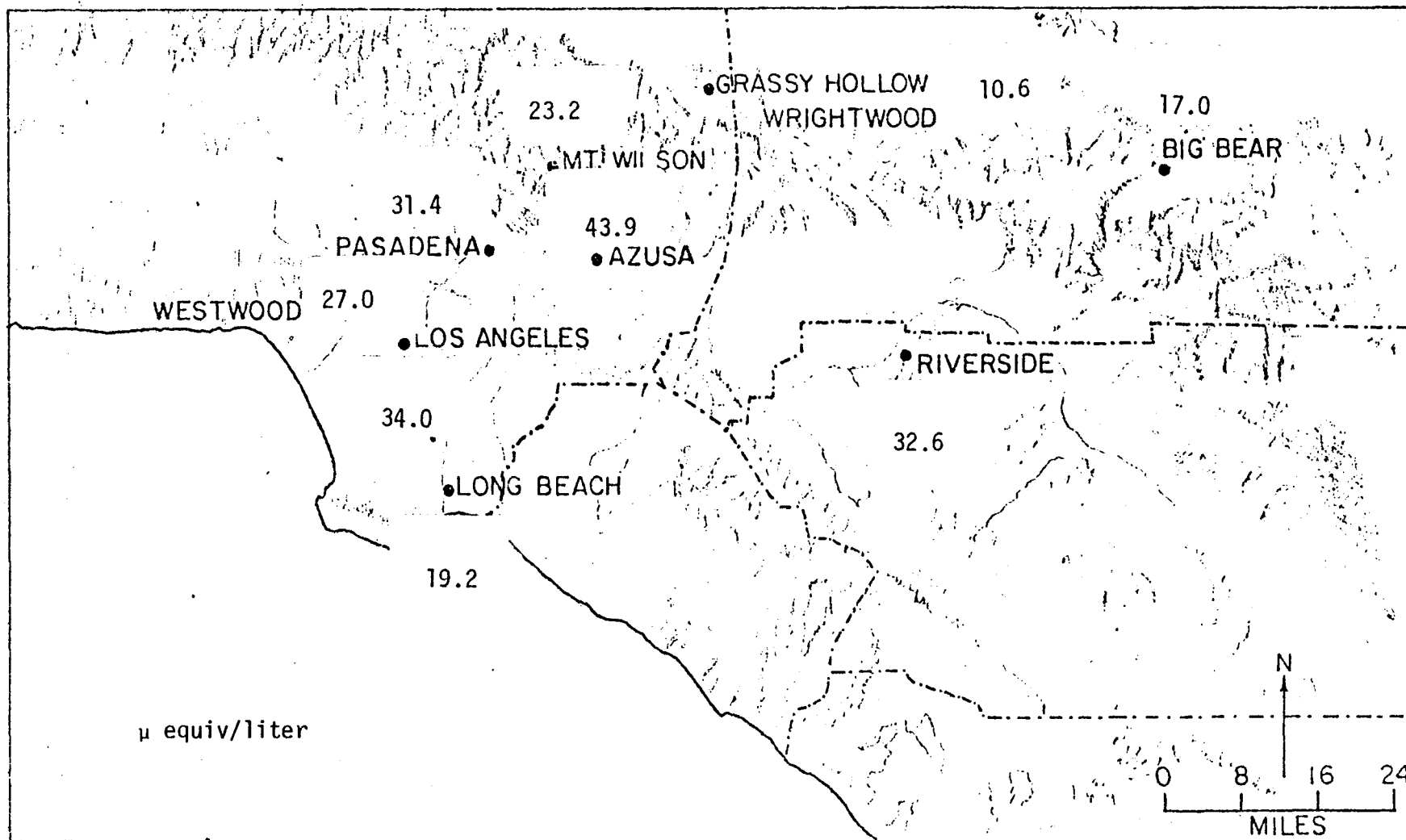


Figure 6. Mean Nitrate Values. Fall 1978 - Spring 1979

Table 1

Precipitation Sample Locations

Pasadena

California Institute of Technology
W. M. Keck Laboratory Roof

Azusa

California Institute of Technology
Azusa Laboratory Roof

Big Bear Lake

Big Bear Observatory
West of Observatory

Los Angeles

University of Southern California
Biegler Hall Roof

Long Beach

California State University
Science Building I Roof

Mount Wilson

Mount Wilson Observatory
Southwest of Machine Shop

Riverside

University of California at Riverside
Chemistry Building Roof

Westwood

University of California at Los Angeles
Geology Building Roof

Wrightwood

Grassy Hollow Park
Northwest of Picnic Area

Table 2

Extent of Total Sampling Program at Nine Locations

<u>Location</u>	<u>Dates of Sampling</u>	<u>Storms</u>	<u>Samples</u>	<u>Total Precipitation inches (cm)</u>	
Pasadena	1/4/78 - 3/29/79	38	198	58.0	(147.3)
Azusa	11/10/78 - 3/29/79	17	41	23.0	(58.4)
Big Bear Lake	1/31/79 - 3/29/79	9	12	10.7	(27.2)
Los Angeles	11/10/78 - 3/29/79	17	44	19.4	(49.3)
Long Beach	2/13/79 - 3/29/79	6	20	6.3	(16.0)
Mt. Wilson	10/19/78 - 3/29/79	18	57	43.7	(111.0)
Riverside	11/10/78 - 3/29/79	17	42	13.6	(34.5)
Westwood	1/12/78 - 3/29/79	38	68	54.0	(137.2)
Wrightwood	1/4/78 - 3/29/79	34	51	103	(262)

Mean* Acidities and pH Values for Fall 1978 - Spring 1979

Location	Dates	Storms	Samples	Mean pH	Mean Acidity \pm S.D. [†] (μ eq/liter)	pH Range	Acidity Range (μ eq/liter)
Pasadena	9/1/78-3/29/79	18	79	4.41	38.4 \pm 4.6	2.89 - 6.24	1600 -(-8.1)
Azusa	11/10/78-3/29/79	17	41	4.66	21.6 \pm 3.8	3.56 - 5.86	277 -(-2.3)
Big Bear Lake	1/31/79-3/29/79	9	12	5.42	2.45 \pm 2.1	4.51 - 6.45	308 -(-13.9)
Los Angeles	11/10/78-3/29/79	17	44	4.49	32.0 \pm 3.7	3.92 - 5.43	121 -(2.3)
Long Beach	2/5/79-3/29/79	6	20	4.54	28.5 \pm 7.3	3.96 - 5.29	110 -(4.2)
Mt. Wilson	10/10/78-3/29/79	18	57	4.99	9.87 \pm 3.0	3.86 - 7.00	137 -(-50)
Riverside	11/10/78-3/29/79	17	42	4.97	10.3 \pm 2.2	4.25 - 6.44	57 -(-13.4)
Westwood	9/1/78-3/29/79	20	50	4.53	29.5 \pm 3.2	3.91 - 5.77	124 -(-1.3)
Wrightwood	12/3/78-3/29/79	16	24	4.90	12.2 \pm 1.8	4.54 - 5.41	29 -(2.6)

*Precipitation-weighted mean hydrogen-ion concentrations and acidities. The mean defined in this way is the chemical flux \div water flux, and thus represents the average loading concentrations.

[†]Standard deviation.

SITE

	Long Beach	Mt. Wilson	Pasadena (Caltech)	Westwood (UCLA)	Riverside (UCR)	Los Angeles (USC)	Wrightwood	Big Bear Lake
Azusa	n.s.	>95%	>99%	n.s.	>95%	n.s.	>95%	>99%
Long Beach		>95%	n.s.	n.s.	>95%	n.s.	>95%	>99%
Mt. Wilson			>99%	>99%	n.s.	>99%	n.s.	>95%
Pasadena				n.s.	>99%	n.s.	>99%	>99%
Westwood (UCLA)					>99%	n.s.	>99%	>99%
Riverside (UCR)						>99%	n.s.	>95%
Central L.A. (USC)							>99%	>99%
Wrightwood - Grassy Hollow								>99%

Table 4. Significance of the Difference in Mean pH for Each Pair of Sampling Sites

Los Angeles Basin Fall 1978 - Spring 1979

Table 5
pH and Precipitation Data at Nine Locations
March 13 to March 21, 1979

Location	Period	pH	Precipitation (in)
Pasadena	3-14 to 3-21	4.22	0.24
		4.35	0.24
		4.60	0.25
		3.97	0.23
		3.79	0.24
		4.17	0.24
		4.38	0.11
		4.18	0.24
		4.49	0.03
		4.00	0.13
Azusa	3-13 to 3-20	4.02	0.24
		4.91	0.24
		5.37	0.24
		4.43	1.11
Mt. Wilson	3-14 to 3-21	4.38	0.24
		4.41	0.24
		4.71	0.24
		4.49	0.72
		4.88	0.66
		7.00	0.78
		6.86	0.62
Los Angeles	3-14 to 3-21	4.45	0.24
		3.92	0.24
		4.11	0.24
		4.19	0.35
		4.11	0.07
		4.43	0.24
		4.97	0.24
Westwood	3-14 to 3-21	3.97	0.24
		4.44	0.24
		4.50	0.24
		4.22	0.24
		4.42	0.24
		4.70	0.24
		4.72	0.24

Table 5 (continued)

Location	Period	pH	Precipitation (in)
Long Beach	3-14 to 3-21	4.51	0.24
		4.51	0.24
		4.19	0.24
		4.88	0.71
		4.94	0.45
Riverside	3-13 to 3-20	4.61	0.24
		4.82	0.24
		4.79	0.24
		4.40	0.55
		4.35	0.19
Wrightwood	3-13 to 3-20	4.57	1.05
		4.68	1.04
		4.65	1.32
		5.26	1.28
Big Bear	3-13 to 3-20	4.51	1.18
		4.88	1.50
		5.90	1.14

Table 6A

Mean Concentrations in Precipitation at Pasadena

January-August 1978

20 storms, 34.8 inches of precipitation, 119 samples

Cation	<u>Concentration</u>		Anion	<u>Concentration</u>	
	mg/ℓ	μ equiv/ℓ		mg/ℓ	μ equiv/ℓ
NH ₄ ⁺	0.292	16.2	Cl ⁻	0.843	23.8
Na ⁺	0.467	20.3	NO ₃ ⁻	1.41	22.7
K ⁺	0.0537	1.37	SO ₄ ²⁻	1.78	37.2
Ca ²⁺	0.142	7.08	F ⁻		<1
Mg ²⁺	0.0744	6.12	Br ⁻		0.28
H ⁺		33.8	H ₂ PO ₄ ⁻	<0.005	<0.15
			HCO ₃ ⁻		<u>0.148</u>
total cations		84.87	total anions		84.13

Mean pH	4.47	
Organic carbon	1.69	mg/ℓ
Total phosphate	1.10	μg/ℓ
Suspended solids	1.44	mg/ℓ

Table 6B

Mean Concentrations in Precipitation at Pasadena

September 1978 - March 1979

18 storms, 23.2 inches of precipitation, 79 samples

Cation	<u>Concentration</u>		Anion	<u>Concentration</u>	
	mg/l	μ equiv/l		mg/l	μ equiv/l
NH ₄ ⁺	0.379	21.1	Cl ⁻	0.998	28.1
Na ⁺	0.553	24.0	NO ₃ ⁻	1.94	31.4
K ⁺	0.0657	1.68	SO ₄ ²⁻	1.85	38.5
Ca ²⁺	0.133	6.66	F ⁻		<1
Mg ²⁺	0.0869	7.15	Br ⁻		0.25
H ⁺		38.5	H ₂ PO ₄ ⁻	<0.005	<0.15
			HCO ₃ ⁻		0.13
total cations		99.09	total anions		98.38

Mean pH	4.41	
Organic carbon	3.09	mg/l
Total phosphate	0.671	μg/l
Suspended solids	2.80	mg/l

Table 7

Mean Concentrations in Precipitation at Azusa

November 1978 - March 1979

17 storms, 23 inches of precipitation, 41 samples

Cation	<u>Concentration</u>		Anion	<u>Concentration</u>	
	mg/ℓ	μ equiv/ℓ		mg/ℓ	μ equiv/ℓ
NH_4^+	0.651	36.2	Cl^-	0.992	28.0
Na^+	0.550	23.9	NO_3^-	2.72	43.9
K^+	0.0667	1.71	SO_4^{2-}	1.81	37.7
Ca^{2+}	0.307	15.3	F^-		< 1
Mg^{2+}	0.0972	8.00	Br^-		0.37
H^+		21.8	H_2PO_4^-	<0.005	<0.15
		<hr/>	HCO_3^-		<hr/> 0.23
total cations		106.91	total anions		110.20

Mean pH	4.66	
Organic carbon	6.59	mg/ℓ
Total phosphate	0.274	mg/ℓ
Suspended solids	9.23	mg/ℓ

Table 8

Mean Concentrations in Precipitation at Big Bear Lake

January 1979 - March 1979

9 storms, 10.7 inches of precipitation, 12 samples

Cation	<u>Concentration</u>		Anion	<u>Concentration</u>	
	mg/ℓ	μ equiv/ℓ		mg/ℓ	μ equiv/ℓ
NH_4^+	0.134	7.467	Cl^-	0.185	5.21
Na^+	0.0966	4.20	NO_3^-	1.054	17.0
K^+	0.0172	0.440	SO_4^{2-}	0.311	6.47
Ca^{2+}	0.186	9.26	F^-		< 1
Mg^{2+}	0.0916	7.54	Br^-		0.019
H^+		3.78	H_2PO_4^-	< 0.005	< 0.15
			HCO_3^-		<u>1.32</u>
total cations		32.69	total anions		30.02
		Mean pH			5.42

Table 9

Mean Concentrations in Precipitation at Los Angeles

November 1978 - March 1979

17 storms, 19.4 inches of precipitation, 44 samples

Cation	<u>Concentration</u>		Anion	<u>Concentration</u>	
	mg/ℓ	μ equiv/ℓ		mg/ℓ	μ equiv/ℓ
NH_4^+	0.647	35.9	Cl^-	1.42	40.0
Na^+	0.785	34.1	NO_3^-	2.11	34.0
K^+	0.191	4.88	SO_4^{2-}	2.67	55.5
Ca^{2+}	0.292	14.6	F^-		< 1
Mg^{2+}	0.128	10.6	Br^-		0.57
H^+		32.1	H_2PO_4^-	<0.005	<0.15
			HCO_3^-		<u>9.16</u>
total cations		132.2	total anions		130.2

Mean pH	4.49
Organic carbon	3.39 mg/ℓ
Total phosphate	0.0923 mg/ℓ
Suspended solids	6.45 mg/ℓ

Table 10

Mean Concentrations in Precipitation at Long Beach

February 1979 - March 1979

6 storms, 6.3 inches of precipitation, 20 samples

Cation	<u>Concentration</u>		Anion	<u>Concentration</u>	
	mg/ℓ	μ equiv/ℓ		mg/ℓ	μ equiv/ℓ
NH ₄ ⁺	0.257	14.3	Cl ⁻	1.47	41.5
Na ⁺	0.855	37.2	NO ₃ ⁻	1.19	19.2
K ⁺	0.0376	0.961	SO ₄ ²⁻	2.44	50.9
Ca ²⁺	0.177	8.82	F ⁻		<1
Mg ²⁺	0.128	11.4	Br ⁻		0.21
H ⁺		28.7	H ₂ PO ₄ ⁻	<0.005	<0.15
			HCO ₃ ⁻		<u>0.18</u>
total cations		101.4	total anions		113.0

Mean pH	4.54
Organic carbon	3.27 mg/ℓ
Total phosphate	0.019 mg/ℓ
Suspended solids	6.04 mg/ℓ

Table 11

Mean Concentrations in Precipitation at Mt. Wilson

October 1978 - March 1979

18 storms, 43.7 inches of precipitation, 57 samples

Cation	<u>Concentration</u>		Anion	<u>Concentration</u>	
	mg/ℓ	μ equiv/ℓ		mg/ℓ	μ equiv/ℓ
NH ₄ ⁺	0.640	35.5	Cl ⁻	0.986	27.8
Na ⁺	0.587	25.5	NO ₃ ⁻	1.44	23.2
K ⁺	0.0668	1.71	SO ₄ ²⁻	1.90	39.7
CA ²⁺	0.187	9.34	F ⁻		< 1
Mg ²⁺	0.0804	6.62	Br ⁻		0.17
H ⁺		10.35	H ₂ PO ₄ ⁻	<0.005	<0.15
		_____	HCO ₃ ⁻		<u>0.484</u>
total cations		89.0	total anions		91.4
		Mean pH		4.99	
		Organic carbon		6.3 mg/ℓ	
		Total phosphate		0.260 mg/ℓ	
		Suspended solids		9.46 mg/ℓ	

Table 12

Mean Concentrations in Precipitation at Riverside

November 1978 - March 1979

17 storms, 13.6 inches of precipitation, 42 samples

Cation	<u>Concentration</u>		Anion	<u>Concentration</u>	
	mg/ℓ	μ equiv/ℓ		mg/ℓ	μ equiv/ℓ
NH ₄ ⁺	0.601	33.7	Cl ⁻	1.06	30.0
Na ⁺	0.578	25.1	NO ₃ ⁻	2.02	32.6
K ⁺	0.0943	2.41	SO ₄ ²⁻	1.60	33.4
Ca ²⁺	0.345	17.2	F ⁻		< 1
Mg ²⁺	0.102	8.37	Br ⁻		0.17
H ⁺		10.74	H ₂ PO ₄ ⁻	< 0.005	< 0.15
		_____	HCO ₃ ⁻		<u>0.467</u>
total cations		97.5	total anions		96.6
		Mean pH		4.97	
		Organic carbon		4.25 mg/ℓ	
		Total phosphate		0.189 mg/ℓ	
		Suspended solids		6.13 mg/ℓ	

Table 13A

Mean Concentrations in Precipitation at Westwood

January 1978 - August 1978

18 storms, 33.5 inches of precipitation, 18 samples

Cation	<u>Concentration</u>		Anion	<u>Concentration</u>	
	mg/l	μ equiv/l		mg/l	μ equiv/l
NH_4^+	0.227	12.6	Cl^-	1.37	42.1
Na^+	0.789	34.3	NO_3^-	0.599	9.66
K^+	0.0250	0.640	SO_4^{2-}	1.21	25.2
Ca^{2+}	0.0912	4.55	F^-		< 1
Mg^{2+}	0.114	9.40	Br^-		0.22
H^+		16.0	H_2PO_4^-	<0.005	<0.15
		_____	HCO_3^-		<u>0.31</u>
total cations		77.5	total anions		77.5
Mean pH		4.80			

Table 13B

Mean Concentrations in Precipitation at Westwood

September 1978 - March 1979

20 storms, 20.5 inches of precipitation, 50 samples

Cation	<u>Concentration</u>		Anion	<u>Concentration</u>	
	mg/ℓ	μ equiv/ℓ		mg/ℓ	μ equiv/ℓ
NH ₄ ⁺	0.375	20.8	Cl ⁻	1.16	32.6
Na ⁺	0.664	28.9	NO ₃ ⁻	1.68	27.0
K ⁺	0.595	1.52	SO ₄ ²⁻	2.04	42.4
Ca ²⁺	0.205	10.2	F ⁻		< 1
Mg ²⁺	0.106	8.75	Br ⁻		0.42
H ⁺		29.65	H ₂ PO ₄ ⁻	<0.005	<0.15
			HCO ₃ ⁻		<u>0.17</u>
total cations		99.8	total anions		102.6

Mean pH 4.53

Organic carbon 4.243 mg/ℓ

Total phosphate 0.294 mg/ℓ

Suspended solids 4.347 mg/ℓ

Table 14A

Mean Concentrations in Precipitation at Wrightwood

January 1978 - August 1978

18 storms, 55 inches of precipitation, 27 samples

Cation	<u>Concentration</u>		Anion	<u>Concentration</u>	
	mg/l	μ equiv/l		mg/l	μ equiv/l
NH_4^+	0.00156	0.086	Cl^-	0.0597	1.68
Na^+	0.0314	1.37	NO_3^-	0.0487	0.786
K^+	0.00313	0.080	SO_4^{2-}	0.0722	1.50
Ca^{2+}	0.078	3.90	F^-		< 1
Mg^{2+}	0.0193	1.58	Br^-		0.024
H^+		1.24	H_2PO_4^-	<0.005	<0.15
			HCO_3^-		<u>4.03</u>
total cations		8.26	total anions		8.03

Mean pH 5.91

Table 14B

Mean Concentrations in Precipitation at Wrightwood

December 1978 - March 1979

16 storms, 48 inches of precipitation, 24 samples

Cation	<u>Concentration</u>		Anion	<u>Concentration</u>	
	mg/l	μ equiv/l		mg/l	μ equiv/l
NH_4^+	0.0156	0.864	Cl^-	0.179	5.05
Na^+	0.0935	4.07	NO_3^-	0.657	10.6
K^+	0.00939	0.240	SO_4^{2-}	0.345	7.18
Ca^{2+}	0.0782	3.90	F^-		< 1
Mg^{2+}	0.0204	1.68	Br^-		0.032
H^+		12.56	H_2PO_4^-	<0.005	<0.015
			HCO_3^-		<u>0.399</u>
total cations		23.31	total anions		23.26
Mean pH			4.90		

Table 15

Variations in pH, Nitrate, Nitrite and Sulfate

during a Storm of High Intensity at Pasadena

February 28 - March 2, 1978

Precipitation ~ 8 1/4 inches

25 samples

Date	Hour	Intensity in/hr	NO ₃ ⁻ μM*	NO ₂ ⁻ μM	SO ₄ ²⁻ μM	pH
2-28-78	0300	0.062	29.9	5.3	24.3	4.52
	1200	0.225	15.0	0.7	10.8	4.79
	1405	0.231	10.5	0.4	7.4	5.46
	1500	0.694	4.6	0.4	3.3	5.35
	1550	0.938	8.4	0	7.5	5.61
	1625	0.375	4.0	0.9	2.7	6.05
	1645	3.000	11.7	0	11.6	6.24
	1730	0.214	3.6	0	2.4	5.63
	1830	0.375	3.2	0.3	1.2	5.61
	2359	0.250	2.0	1.6	1.7	5.74
3-1-78	0110	0.250	2.7	2.3	1.7	5.57
	0130	0.500	6.1	0	6.7	5.54
	0232	0.563	2.3	0	2.4	5.69
	0300	0.500	2.0	0	0.9	5.62
	0537	1.500	7.1	0	10.2	5.29
	0959	1.500	9.8	0.2	9.4	5.14
	1050	3.000	7.0	0.3	5.4	5.48
	1200	0.281	10.9	0.2	12.7	4.64
	1320	0.179	20.5	0	22.5	4.49
	1540	0.300	7.8	0.4	14.0	4.59
3-2-78	1830	0.275	38.5	0	39.3	4.08
	2337	0.189	25.1	1.1	28.8	4.37
	0400	0.125	30.6	5.4	26.8	4.23
	0930	0.129	32.8	5.3	37.5	4.21
	1200	0.179	24.6	0.5	23.8	4.35

* μM is micromoles/liter

Table 16

Variations in pH, Nitrate and Sulfate during
 a Storm of Moderate Intensity at Pasadena
 January 14-16, 1979

Precipitation ~ 2 1/4 inches

5 Samples

Date	Hour	Intensity in/hr	NO_3^- μM^*	NO_3^- μM	pH
1-14-79	0800	0.100	49.7	34.2	4.19
1-15-79	0700	0.500	16.7	16.6	4.48
1-15-79	1030	0.136	4.3	14.7	4.58
1-15-79	2200	0.139	3.1	12.3	4.74
1-16-79	0445	0.267	7.1	7.9	4.83

* μM is micromoles/liter

Table 17

Variations in pH, Nitrate and Sulfate during
 a Storm of Moderate Intensity at Pasadena
 February 20-21, 1979
 Precipitation ~ 2 inches
 6 Samples

Date	Hour	Intensity in/hr	NO ₃ ⁻ μM *	SO ₄ ²⁻ μM	pH
2-20-79	1630	0.083	62.9	35.0	4.05
2-20-79	2115	0.100	14.2	7.2	4.69
2-21-79	0015	0.167	12.2	13.8	4.43
2-21-79	0200	0.600	7.5	8.6	4.72
2-21-79	1300	0.250	26.6	20.7	4.43
2-21-79	1700	0.250	20.6	12.3	4.61

*μM is micromoles/liter

Table 18

Chemical Data for Small Rainfall Increments
 following Periods of No Rainfall
 Pasadena

Date	Hour	Increment (in)	Prior Period (days)	pH	NO ₃ ⁻ μM*	SO ₄ ²⁻ μM*
3-11-78	1030	3/16	7	3.87	263	33
4-25-78	0900	3/16	10	3.84	47	55
9-7-78	0800	<1/1000	1	2.89	1094	157
12-01-78	0800	1/10	11	3.23	601	133
1-08-79	1700	<1/8	3	3.85	109	42
1-28-79	0800	<1/8	10	3.70	251	39
3-13-79	0800	<1/8	12	3.72	183	69

*μM is micromoles/liter